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EVALUATION OF DEWATERING OF LIMESTONE WET SCRUBBING PROCESS SLUDGES

West Virginia University

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Limestone Wet Scrubbing Process Sludges

Environmental Protection Agency
Research Triangle Park, N.C. 27711

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Flocculating
Injection
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Sulfur Oxides
Sand Filtration
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By

Coal Research Bureau
West Virginia University
Morgantown, West Virginia 26505

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ABSTRACT

Several methods of dewatering solid materials were applied on a bench scale to wet-collected, limestone-modified flyash from a coal-fired electric power plant using limestone-injection and wet-scrubbing methods to control the emission of gaseous sulfur oxides. Porous-bed sand filtration, lagooning and possibly pressure filtration appear to hold the most promise. Aluminum extraction tests using sodium hydroxide, sodium carbonate and combinations of the two yielded less than 50 percent of the aluminum available in the leach liquor while structural materials testing indicated that there is insufficient free lime available in the modified ash to act as a suitable binding agent.

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INTRODUCTION

The purpose of the subject contract has been to investigate the potential utilization of wet-collected, limestone or dolomite-modified flyashes resulting from sulfur dioxide control methods. Specific areas under investigation have included dewatering, alumina leaching, and production of structural products by employing potential cementitious properties of the modified flyashes. In addition, literature surveys have been made to aid in the determination of the state of the art and how it may be applied for each particular area.

The studies conducted under this contract (EHS-D-71-11) are complimentary to three previous studies under Contracts CPA 70-66, PH 86-67-122 and PH 22-68-18. All contracts have been concerned with various aspects of characterization and utilization of wet- or dry-collected modified flyash. However, owing to a scarcity of wet collected modified flyash samples, the data reported in this study have been obtained using material generated by the Combustion Engineering limestone-injection, wet-collection process at the Lawrence Station of the Kansas Power and Light Co. (KPL).

DEWATERING STUDIES

Potential utilization of wet-collected modified flyash will be dependent in part upon the successful dewatering of this material. Also, disposal will be facilitated if the water can be removed from the ash materials and returned to the power station for recycling.

The modified flyash used in this program is a wet-collected limestone material and contains approximately 1/2 to 2 percent solid materials, 85 percent of which is smaller than 50 microns. With time, natural sedimentation processes yield a sludge which may contain 50 to 60 percent solids. This figure is misleading; however, as layering occurs and it appears that chemical reaction, eg, hydration, etc may account for the removal of a portion of the interstitial and intralayer waters. Disturbance of the sediments, such as would occur during dredging operations, allows any water remaining in the pond area to remix with the flyash and produce a slurry with 20-45 percent solids.

A. Literature Studies. In order to properly define specific areas to be investigated in the potential dewatering of modified flyash slurries, a literature study (see Appendix A) was undertaken. Based upon information obtained in this study, the following dewatering processes and aids were selected for bench-scale laboratory examination:

a) filtration

b) coagulation, and

c) flocculation.

Filtration was chosen as it is a commonly used dewatering method for fine particles. The literature study indicated that vacuum and pressure filtration methods were most feasible. Further, it was decided that dewatering aids such as flocculants and coagulants should also be examined to provide basic information for other dewatering processes. In order to differentiate between the two sometimes interchangeably used terms, coagulants were considered as salts which alter the surface charge of individual colloidal size particles to lower their repulsive effects while flocculants were considered to be long-chain polymers which actually form "bridges" between particles. In either case, a grouping together of particles to aid in settling or

filtration was the goal.

B. Pressure Filtration was selected for laboratory study because preliminary work had indicated that modified flyash slurries might prove amenable to such a dewatering method. A 3 5/8 inch square laboratory scale pressure filter was obtained through D. R. Sperry and Company* and tests were performed to determine the effects of such parameters as slurry concentration, gas pressure, and cycle duration between filter cake removal upon the solids content of the final filter cake.

Initial tests indicated that varying the solids content of the slurry had little effect upon the final filter cake as long as the slurry content was below 10-15 percent solids. Accordingly, the slurry concentration was maintained between 2 1/2 and 3 percent solids as this was estimated to be the highest obtainable during normal operation of the scrubbing system at Kansas Power and Light Co. The filtration pressure levels examined were 60, 80 and 100 psig held for two-hour intervals for each test run. At the end of each test, the filter cake was examined and the volume of filtrate recovered was measured. The two-hour test duration period was selected as it represents a typical operating cycle between filter change and service for a commercial pressure filter operation. Compressed air was used to provide the necessary pressure in all of the tests.

Because the capacity of the laboratory apparatus was insufficient to allow a two-hour test run, it had to be opened and refilled several times during each run. Extreme care was taken to ensure that the existing cake was not disturbed or allowed to dry as cracking of the filter cake would effectively terminate the test run. The volume of filtrate recovered was plotted

*The use of commercial firm or trade names does not imply endorsement by the Coal Research Bureau, but is simply intended for clarification or description of the equipment used.

as a function of time for each test performed. Two representative curves are included as Figure 1. The even filtering rate with respect to time as shown by the curves indicate that the filter was not blinding* and also that there was very little difference when the pressure was increased from 80 to 100 psig. Representative data from the tests performed is included below:

TABLE 1

PRESSURE FILTRATION CHARACTERISTICS OF KPL SLURRY

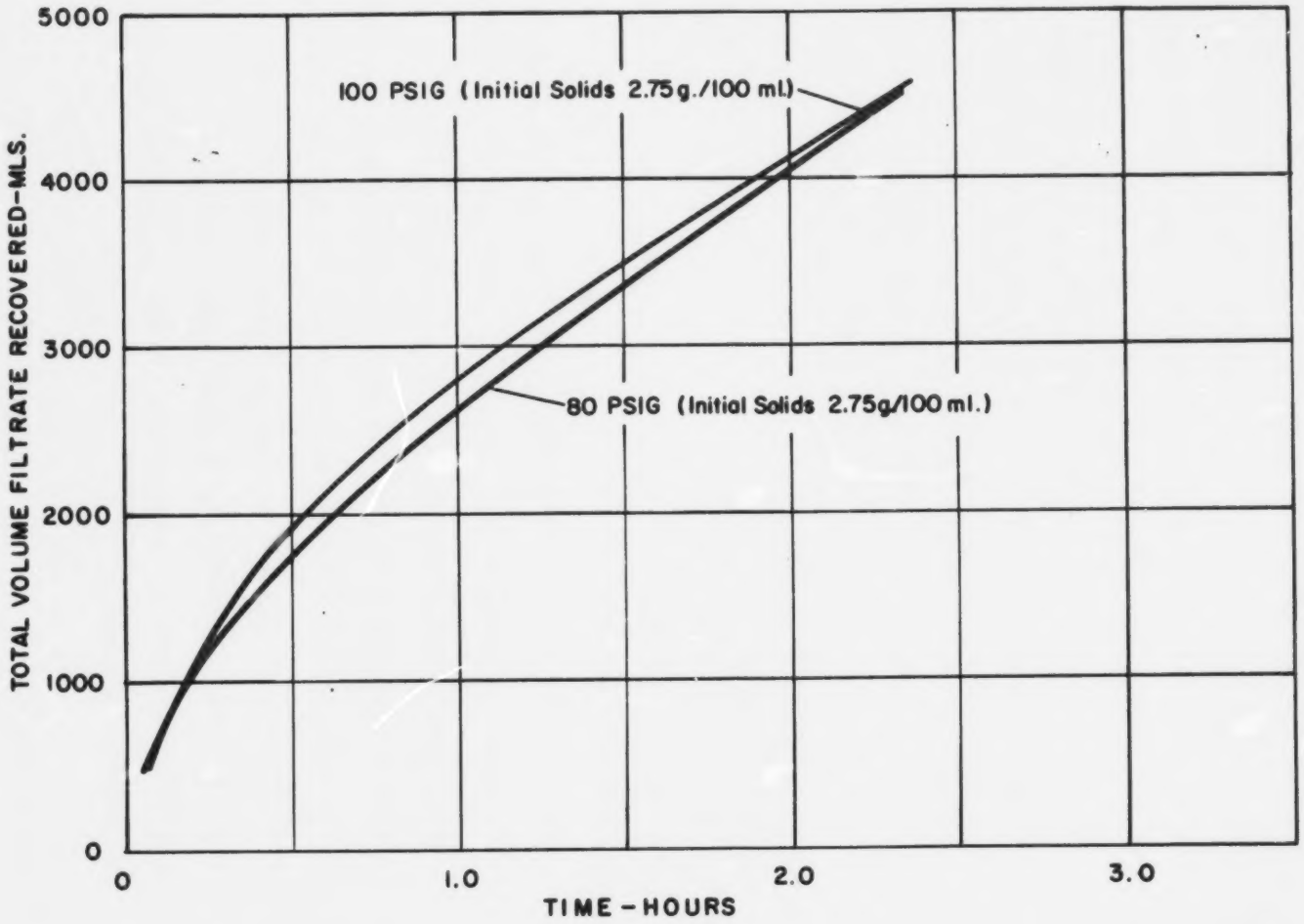
Pressure (psig)	Percent Solids (Initial)	Slurry Volume (Gallons)	Filtrate Volume (Gallons)	Filtrate Slurry Ratio	Filter Cake % Solids	Hours
60	2.60	1.32	1.18	0.89	34.5	2
80	2.60	1.39	1.26	0.90	33.0	2
100	2.50	1.24	1.10	0.88	34.0	2
80	2.75	1.26	1.13	0.89	35.0	2
100	2.75	1.29	1.15	0.89	36.0	2
100	2.55	1.88	1.73	0.92	39.0	4

The results of the pressure filtration tests indicate that modified flyash slurries could be dewatered to produce a filter cake containing 35 to 40 percent solids. The water volume recovered by such a method is approximately 90 percent of the original slurry volume. It would be satisfactory for recycling as it is very clear and the addition of reagents such as flocculants should not be necessary for further clarification. Other tests performed indicate that blinding of the filter cake does not occur within 10 hours of operation and that the length of the filtering cycle would be determined by the capacity of the filter apparatus. Economic data was not obtained as it would be dependent upon the particular power plant scrubbing slurry concentration and type of alkaline material used for injection. It also appears probable that the underflow from a classifier-thickener would be amenable for further dewatering by this method. However, additional research is needed in this area.

*Blinding refers to the physical blocking of pore spaces in the filter media by small, solid particles of the material being filtered.

Figure 1

THE EFFECT OF PRESSURE LEVEL UPON THE DEWATERING CAPABILITY OF SPERRY PRESSURE FILTER USING KPL SLURRY



C. Coagulation was examined as a means of increasing the settling rates of the smaller modified ash particles. Although the majority of the ash would settle within 5 to 10 minutes, it was noted that the finer particles remained in suspension, leaving the water cloudy or turbid, for several hours. Zeta potential tests performed upon the modified flyashes indicated that they were already within the range, ± 15 millivolts, in which coagulation should occur. This was verified in the laboratory by adding various concentrations of trivalent, divalent and monovalent inorganic coagulants to the slurry. The resultant data, presented as Table 2, indicated that there were no significant changes affected in the zeta potential of the modified ash particles due to the presence of the coagulants. It was therefore concluded that coagulation of the fine ash particles did not appear promising and the study was terminated.

D. Flocculation and Vacuum Filtration were investigated as a combination method for dewatering modified flyash slurries. Rather than acting primarily to change particle surface charges, flocculants act as physical bridges to bind particles together and their effectiveness is not dependent upon the surface charge of the particles as are coagulants. Flocculants, generally long-chain polymers, are commonly used in conjunction with mechanical dewatering processes and a general testing method has been devised to evaluate the effectiveness of flocculants when used with vacuum filtration. This commonly used test series includes the Buchner funnel test, the vacuum break test and the filter leaf test. The detailed procedures involved in these tests are included in Appendix B.

Buchner Funnel Test

The Buchner funnel test is designed to aid in the selection of a particular flocculant and concentration to provide optimum dewatering of a slurry with the

aid of vacuum filtration. In the subject testing program, a total of thirty-five series of tests were performed with a variety of anionic, non-ionic, and cationic polymers. The average optimum dosage, ie, the dosage which gave the largest volume of filtrate for all thirty-five flocculants, was 3.19 ppm and the average percentage recovery of filtrate was 30.4.

The flocculants studied, their optimum concentrations, and the percentage recovery are presented in Table 3. The primary conclusion to be drawn from the presented data is that the better flocculants were strongly anionic or non-ionic.

Filter Break Test

The filter break test is an extension and refinement of the Buchner funnel test. A flocculated sample of sludge is filtered until it reaches dryness. Air then enters the system through drying cracks or breaks and the vacuum decreases. The time required until the vacuum drops is recorded. This test, however, did not prove to be very precise. The time of break could not in general be determined with high accuracy because the vacuum did not drop noticeably; or, in some cases, did not drop at all. The failure of these tests can probably be attributed to a breaking down of the flocs during filtration and a subsequent "blinding" of the filter media by the smaller (1.0 micron or less) ash particles. An approximate break time was generally measurable and it appeared that the break time for the flocculants examined was between one and three minutes.

The filter break tests were discontinued as the results obtained were not considered precise enough to be meaningful.

Filter Leaf Test

The filter leaf test is designed to reproduce, on a lab-bench scale, the operating cycle of a commercial vacuum filter. Using a series of commercial

TABLE 2

VARIATION OF ZETA POTENTIAL VALUES AS A FUNCTION OF INORGANIC COAGULANT DOSAGE ON WET COLLECTED LIMESTONE MODIFIED FLYASH FROM KANSAS POWER AND LIGHT

Collected October, 1970

Additive	Concentration	Zeta Potential	Specific Cond.	pH
Natural	0	+3	2900	11.3
$Al_2(SO_4)_3$	1 ppm	+3	2600	11.2
	5 ppm	+3	2500	10.8
	10 ppm	+3	2500	10.7
	25 ppm	+2	2500	10.7
	100 ppm	+2	2500	10.7
$BaCl_2$	1 ppm	+3	2700	11.0
	5 ppm	+3	2600	10.9
	25 ppm	+3	2600	10.9
	100 ppm	+2	2400	10.9
KCl	500 ppm	+5	3600	10.7

TABLE 3

VACUUM FILTRATION TEST RESULTS

Flocculant	Type	ppm(1)	% Recovery(2)
Magnifloc 571C	Cationic	0.6	10%
Magnifloc 836A	Anionic	3.8	55%
Calgon 2425	Anionic	5.8	55%
Magnifloc 835A	Anionic	5.8	72%
Magnifloc 560C	Cationic	2.9	27%
Magnifloc 905N	Nonionic	0.19	3%
Magnifloc 837A	Anionic	2.9	26%
Separan AP30	Anionic	2.9	48%
Magnifloc 570C	Cationic	0.1	18%
Separan AP 273	Anionic	4.8	32%
Magnifloc 521C	Cationic	1.0	22%
Hercofloc 827	Nonionic	0.19	40%
Nalcolyte 675	Anionic	3.8	39%
Hercofloc 831	Anionic	1.9	15%
Percol 292	Cationic	2.9	23%
Percol 156	Anionic	5.8	30%
Calgon 240	Anionic	2.9	30%
Nalcolyte 675	Anionic	4.8	43%
Nalcolyte 670	Nonionic	1.9	23%
Reagent S-3595	Anionic	4.8	62%
Drewfloc 230	Anionic	4.8	21%
Hercofloc 827	Nonionic	2.9	60%
Hercofloc 818	Anionic	5.8	23%
Hercofloc 815	Cationic	3.8	18%
Hercofloc 831	Anionic	1.9	33%
Hercofloc 821	Anionic	1.9	19%
Reagent S-3595	Anionic	1.9	99%
Superfloc 127	Nonionic	5	21%
Superfloc 16	Nonionic	4	16%
Superfloc 20	Nonionic	3	4%
Superfloc 84	Nonionic	2	42%
Aerofloc 550	Anionic	4.8	47%
Superfloc 202	Anionic	5	18%
Hercofloc 818	Anionic	2	23%
Zeta Floc S	Cationic	2	7.1%

Average % Recovery = 30.4%
Average Optimum Dosage = 3.19 ppm

Flocculant Type	Average Opt. Conc. PPM	Average % Recovery
Anionic	4.0	36.5
Cationic	1.9	17.9
Nonionic	2.4	26.1

(1) Optimum Concentration

(2) The Percentage Increase of Water Filtered from the Flocculated Slurry in 0.5 Minutes

TABLE 4

DESCRIPTION OF FILTER MEDIA EXAMINED

Eimco Media Number	Weave	Thread Count	Finish	Weight oz/yd^2	Air Flow cfm/ft^2	Yarn Type
NY-529F	2/2 Twill	144 x 54	Heat-Set	8.00	39.65	Multifilament
NY-527F	2/2 Twill	157 x 62	Collandered	5.75	176.00	Monofilament
SFYC-175-211B	Non-Woven	23 mil	----	4.14	44	Cotton
NY-420	1/1 Plain	35 x 35	Stabilized	5.20	---	Multifilament
NY-319F	3/1 Twill	240 x 120	Heat-Set	[illegible].50	4-5	Multifilament
DY-453	2/2 Twill	70 x 38	Grey	14.75	6.97	Spun Staple
NY-306F	1/1 Plain	52 x 39	Heat-Set	5.5	35/40	Multifilament
NY-432	1/1 Plain	60 x 34	Heat-Set	10.00	2.00	Multifilament
NY-384	1/1 Plain	79 x 40	Heat-Set	9.00	6.00	Multifilament
OR-593F	3/1 Twill	48 x 46	Heat-Set Spun	--	73.00	Spun Staple
NY-372	7/1 Satin	60 x 40	Heat-Set	12.00	---	Filament Warp
POPR-858F	2/2 Twill	70 x 32	Greige	12.80	1400	Spun Staple
NY-301	2/2 Twill	54 x 37	Grey	13.30	53.37	Multifilament
CO-12	3/1 Twill	62 x 36	Napped 1/5	10.00	---	Spun Staple
PO-801-RF	1/1 Plain	105 x 40	Grey	9.00	100/150	Monofilament

TABLE 5

FILTER LEAF TEST RESULTS USING CONCENTRATED (10.5 g/100 ml) SLURRY AND 15" Hg VACUUM FILTRATION TIME 1 1/2 MINUTES

Eimco Media Number	Approximate Cake Thickness in Inches	Percent Solids	Comments
NY-529F	0.200	39	350 ml cloudy filtrate
NY-527F	0.160	36	430 ml cloudy filtrate
SFYC-175-211B	0.200	40	360 ml slightly cloudy filtrate
NY-420	---	--	entire sample passed through media
NY-319F	0.120	37	200 ml clear filtrate
DY-453	0.200	39	230 ml slightly cloudy filtrate
NY-306F	0.200	40	350 ml milky filtrate
NY-432	0.240	40	350 ml with large amount of solids
NY-384	0.240	41	310 ml clear filtrate
OR-593F	0.28	39	400 ml clear filtrate
NY-372	0.200	38	320 ml slightly cloudy filtrate
POPR-858F	0.240	35	460 ml clear filtrate
NY-301	0.240	36	430 ml milky filtrate
CO-12	0.200	37	390 ml very clear filtrate
PO-801-RF	0.08	34	200 ml clear filtrate

filter media and a filter leaf apparatus of 0.1 ft^2 area obtained from Eimco Corporation of Salt Lake City, Utah; data was obtained concerning the percent solids in the filter cake, cake-thickness and the volume of filtrate recovered from a slurry containing 10.5 percent solids as recommended by the apparatus manufacturer.

The slurry formed medium sized flocs which disintegrated into fine particles. The cake formed tended to be compact and did not exhibit the degree of cracking which might be expected. Rather, one or two major cracks developed and exhibited slow growth with little branching. A brief description of the various filter media examined is included as Table 4 and the resulting data from these tests are presented in Table 5. This data indicated that the percent moisture in the filter cake is fairly constant regardless of the filter cloth used. The major effects which the different cloths had lay in the areas of filtrate clarity and ease of removal of the filter cake. Also, as indicated in Table 6, a sample of raw sludge subjected to the filter leaf test gave a percentage of water nearly the same as that of sludge treated with flocculant. Another sample of flocculated sludge air-dried for an additional 10 minutes underwent no further appreciable loss of moisture indicating that further dewatering would be difficult.

TABLE 6

COMPARISON OF % MOISTURE IN RAW, 835A-FLOCCULATED AND AIR-DRIED SLUDGES

Sample	Vacuum In. Hg	Cake Thickness (inches)	% Solids
Average for all cloths tested on flocc. slurry	15	0.200	38
Raw sludge	15	0.200	37
Air-dried (10 min)	15	0.240	38

In order to further define the variables involved in vacuum filtration of modified flyash, a series of tests designed to simulate a commercial vacuum filter were performed. The portions of a normal vacuum filter operating cycle investigated included the dip or filter submergence time, the drying time and the cake removal time. The tests consisted of submerging the filter leaf apparatus (see Appendix A) into a 1.3 percent solids modified flyash slurry and determining the volume of filtrate recovered as a function of submergence time. The thickness and percent solids of the filter cake were also monitored. These tests were performed using spun staple and multifilament filter media CO-3 and NY-301 and a vacuum of 28 to 29 inches of mercury. It was found that the filter cake had to accumulate to a thickness of 0.125 inches during the submerged period to permit effective cutting and removal of the dewatered cake. This minimum cake thickness corresponded to a minimum submergence period of four minutes. Included as Table 7 is data which indicates that increasing the submergence period or dip time did not have a significant effect on either the cake thickness or the percent solids of the cake. However, the filtrate volume or the amount of water recovered did increase with time.

TABLE 7

Cloth	Dip Time	Filtrate Vol.	Cake Thickness inches	Drying Time	% Solids
CO-3	4 min	2310	0.18	10 sec	30.7
CO-3	4 min	2150	0.12	60 sec	30.3
CO-3	6 min	2840	0.12	60 sec	31.2
CO-3	8 min	3140	0.12	60 sec	30.4
CO-3	10 min	4170	0.19	60 sec	30.5
NY-301	4 min	2440	0.12	15 sec	30.4
NY-301	6 min	2740	0.19	15 sec	29.4
NY-301	8 min	3240	0.12	15 sec	----
NY-301	4 min	1920	0.12	15 sec	30.2
NY-301	4 min	1990	0.19	120 sec	30.9

In an effort to further examine the effects of reagents upon dewatering, a flocculated and unflocculated sample were examined together. The resulting data are shown in Table 8. It can be seen that the filtrate volume which could be recovered from the flocculated slurry was approximately 50 percent greater than from the raw slurry while the percent solids in the filter cake dropped slightly. Both factors are due to the bridging nature of the flocculants. In the slurry the flocs are light and fluffy allowing the passage of water; while upon drying, the flocs tend to trap and hold water.

TABLE 8

A COMPARISON OF FILTRATE RECOVERY AND CAKE % SOLIDS FOR FILTRATION OF AN UNFLOCCULATED AND FLOCCULATED SLURRY

Filter Media	Slurry Type	Filtrate Vol.	Thickness	% Solids
NY-301	Unflocculated slurry	2235 ml	0.12 inches	31.3
CO-12	Unflocculated slurry	1850	0.19 inches	31.1
NY-301	Flocculated with 835 A	3235	0.16 inches	30.7
CO-12	Flocculated with 835 A	2770	0.22 inches	30.5

These tests indicated that vacuum filtration and possibly flocculation methods are usable with modified flyash slurries. However, due to the large volumes of water passing through the scrubbing system, a preliminary thickening or concentration of the slurry should be effected.

E. Sand Filtration or porous bed filtration was examined as a means of dewatering large volumes of slurry which might exceed the capabilities of conventional equipment. In the laboratory an 11 inch diameter, packed and graded* filter bed of sand and gravel was prepared and approximately 30 liters

*Graded is a geological term meaning vertically sorted particles increasing in size from top to bottom.

of a one percent flyash slurry was introduced on top of the bed. Over 95 percent of the slurry water passed through the filter bed in a short period of time and the cake was allowed to air dry in place. The solids content of the cake with respect to drying duration is shown in Figure 2. The samples taken for percent solids determinations were removed from different locations and care was taken to disturb the drying cake as little as possible. Drying cracks appeared on the 8th day; and by the 20th day, the cake contained 60 percent solids and appeared to have sufficient strength to allow removal on a large scale by common earth moving equipment. In actual practice, this time period would be affected by such positive factors as sunshine and wind and such negative factors as rain and snow. Analyses of the waters were not performed as the quality of the filtrate water would be dependent upon specific slurry and filter bed compositions.

F. Impoundment. Lagoons or settling ponds are likely to be the most commonly used dewatering method for modified flyash. Draining of the lagoon should allow the production of an ash-water slurry containing 50 percent by weight solids. Excess calcium ions in the slurry water react with carbon dioxide in the air and the slurry pH gradually drops from 11.0 to approximately 8.0. The resultant calcium carbonate precipitates out of the water and is collected with the flyash. The settling rate, shown in Figure 3, for KPL slurry was monitored and it was observed that a major portion of the settling occurs within the first 15 minutes of impoundment.

If insufficient land is available for a series of settling lagoons, use of a clarifier-thickner is recommended. Conversations held with engineers of Combustion Engineering, Inc. indicated that slurries with solids contents up to 30 percent by weight could be obtained from the clarifier discharge.

Figure 2

SAND FILTRATION TESTS ON KPL SLURRY

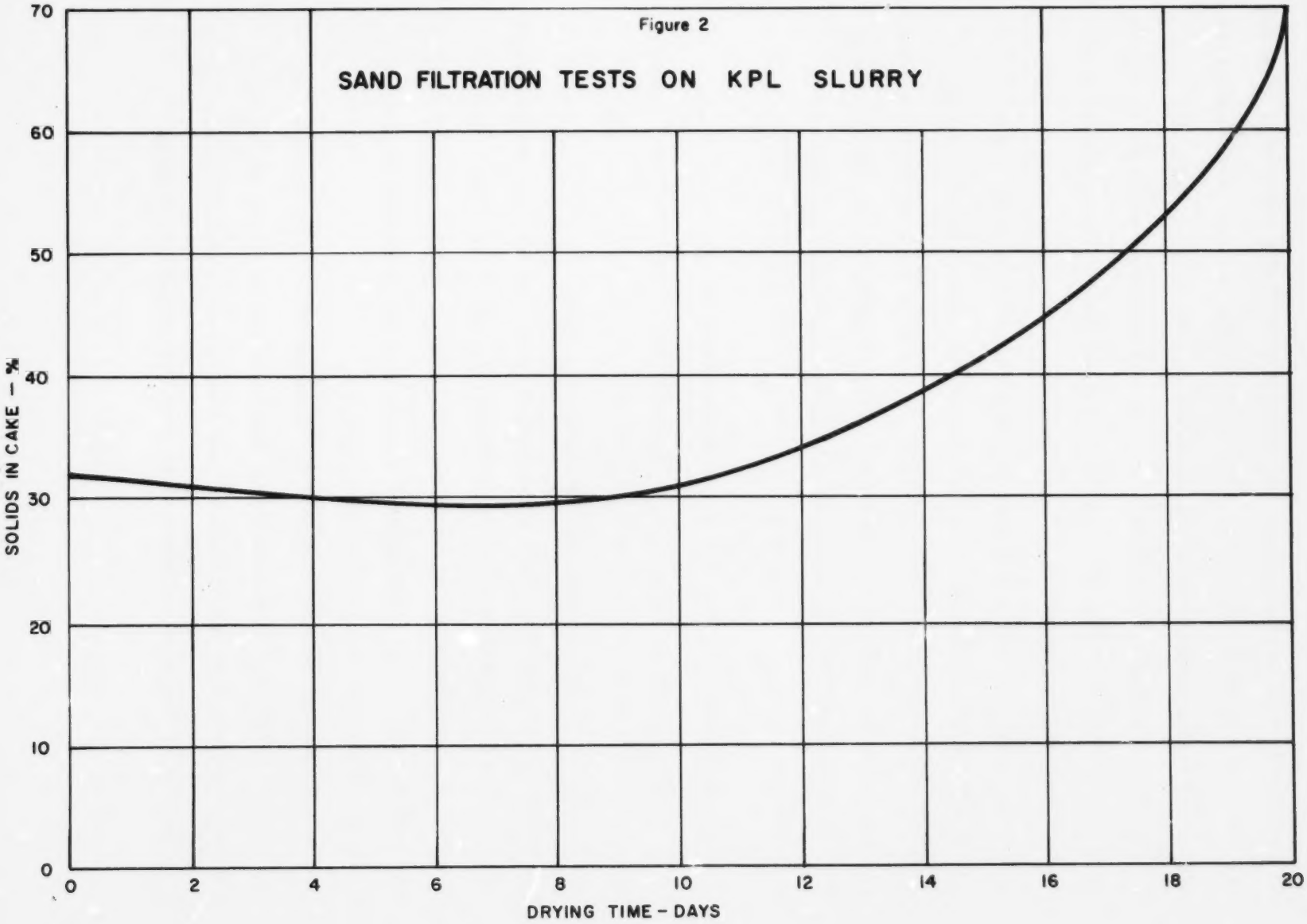
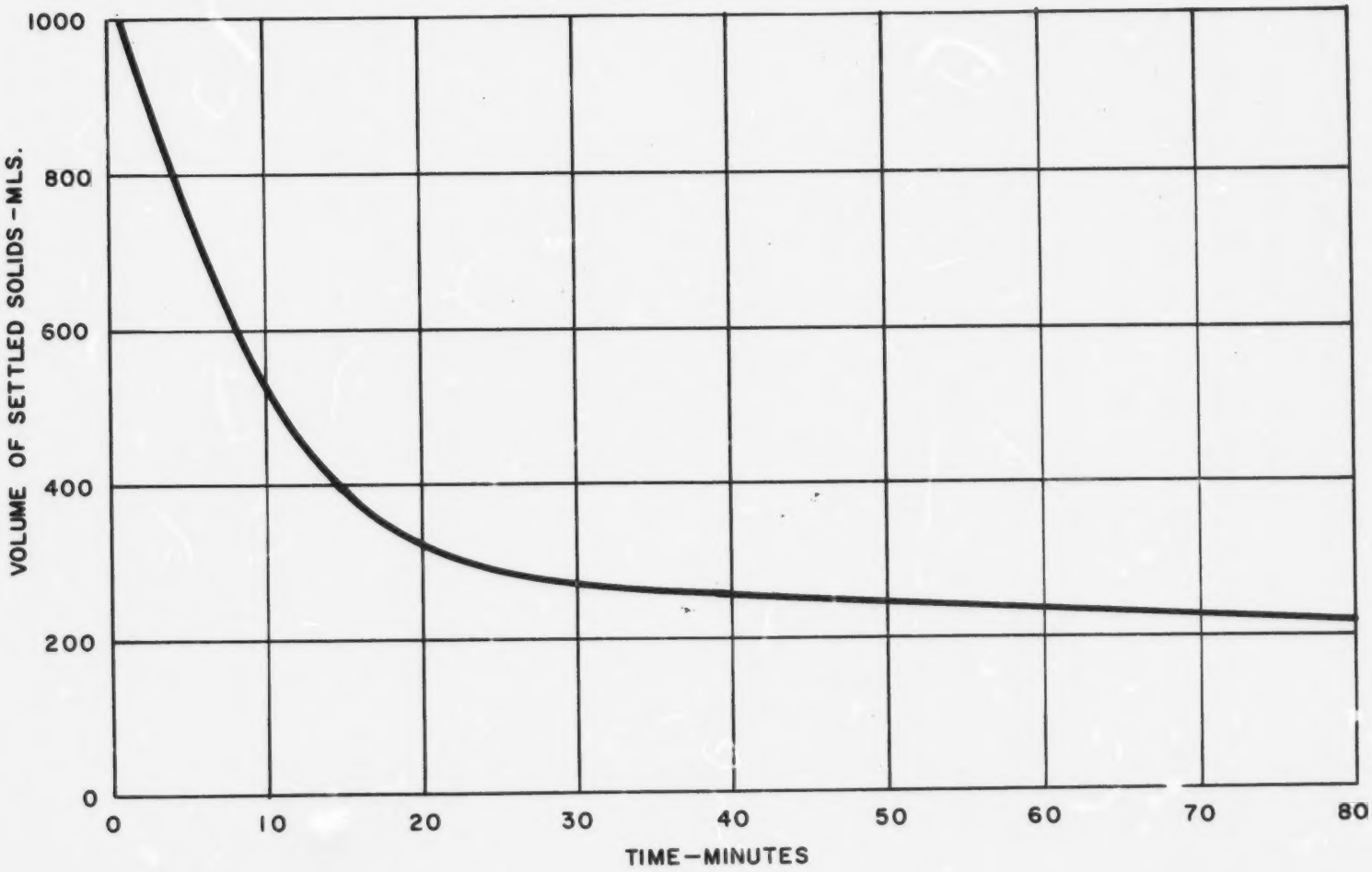


Figure 3

SETTLING TEST OF KPL SLURRY
2.5 Grams Solid/100 Mls. of Slurry



G. Conclusions. A series of graded filter beds prepared from gravel and sand appears to be the most efficient and practical dewatering method for use with wet-collected, limestone-modified flyash. If water-soil interaction is no problem, then a normal settling lagoon such as is currently being used at Kansas Power and Light will provide partial dewatering. Care must be taken, however, to remove all of the water present in the lagoon before cleaning operations begin as remixing with the solids will occur otherwise.

Strongly anionic or non-ionic flocculants were effective and could prove useful if a final water clarification step is desired.

STRUCTURAL PRODUCTS

Potential utilization methods involving wet-collected modified flyash must include some means of either binding the sulfur components in a non-reactive form or recapturing them if an evolution step is involved. Investigations into the pozzolanic activity of wet-collected, limestone-modified flyash indicated that some cementitious activity did occur during such normal sedimentation processes as would exist in a slurry settling pond. A close study of the settled materials indicated that the binding takes place within relatively thin layers of the partially compacted sediments. The binding layers consisted of flyash, growing calcium sulfate crystals and sub-crystalline calcium carbonate. Calcium silicates may have been present as a coating on some flyash particles, but absolute identification by X-ray methods was not possible. Although the binding strength given by the formation of these minerals is quite low, it has proven sufficient in several cases to plug process lines when the power plant slurry flow was stopped for a short time period. Tests performed using 100 percent modified flyash as a concrete mix showed that compressive strengths in the range of 30 to 40 pounds per square inch (psi) occurred. The technical literature was examined to determine whether processes existed which could

enhance the slight natural binding properties of the modified flyash. Because the ash is similar, at least superficially, to the constituents used in the production of autoclaved "sand-lime" (eg, calcium-silicate) structural materials in Europe, it was decided to investigate this potential utilization area. The two major advantages to be found in autoclave processing of modified flyash are:

1. Sulfur gases do not have to be captured and marketed. All of the processing occurs below sulfur dioxide regeneration temperatures; and

2. No pollution problems due to the presence of soluble sulfur compounds have been noted. The sulfur components in autoclaved modified flyash appear to be either chemically combined or bound within the matrix structure of the final structural products.

Prior research, reported in detail in the final report for Contract CPA 70-66 ("Pilot Scale Up of Processes to Demonstrate Utilization of Pulverized Coal Flyash Modified by the Addition of Limestone-Dolomite Sulfur Dioxide Removal Additives"), in the area of utilizing wet-collected modified flyash showed that a very satisfactory calcium-silicate type brick or block could be produced. The raw materials used in the process, shown schematically in Figure 4, consisted, on a dry basis, of 50 percent wet-collected modified flyash (at 34 percent moisture), 11 percent calcium oxide and 39 percent sand. The resultant brick exceeded 4500 psi compressive strength and had an average cold water absorption value of 23 percent with no measurable shrinkage or expansion occurring during autoclaving. These bricks meet ASTM specifications for Grade SW calcium silicate face brick as per specification C73-67.

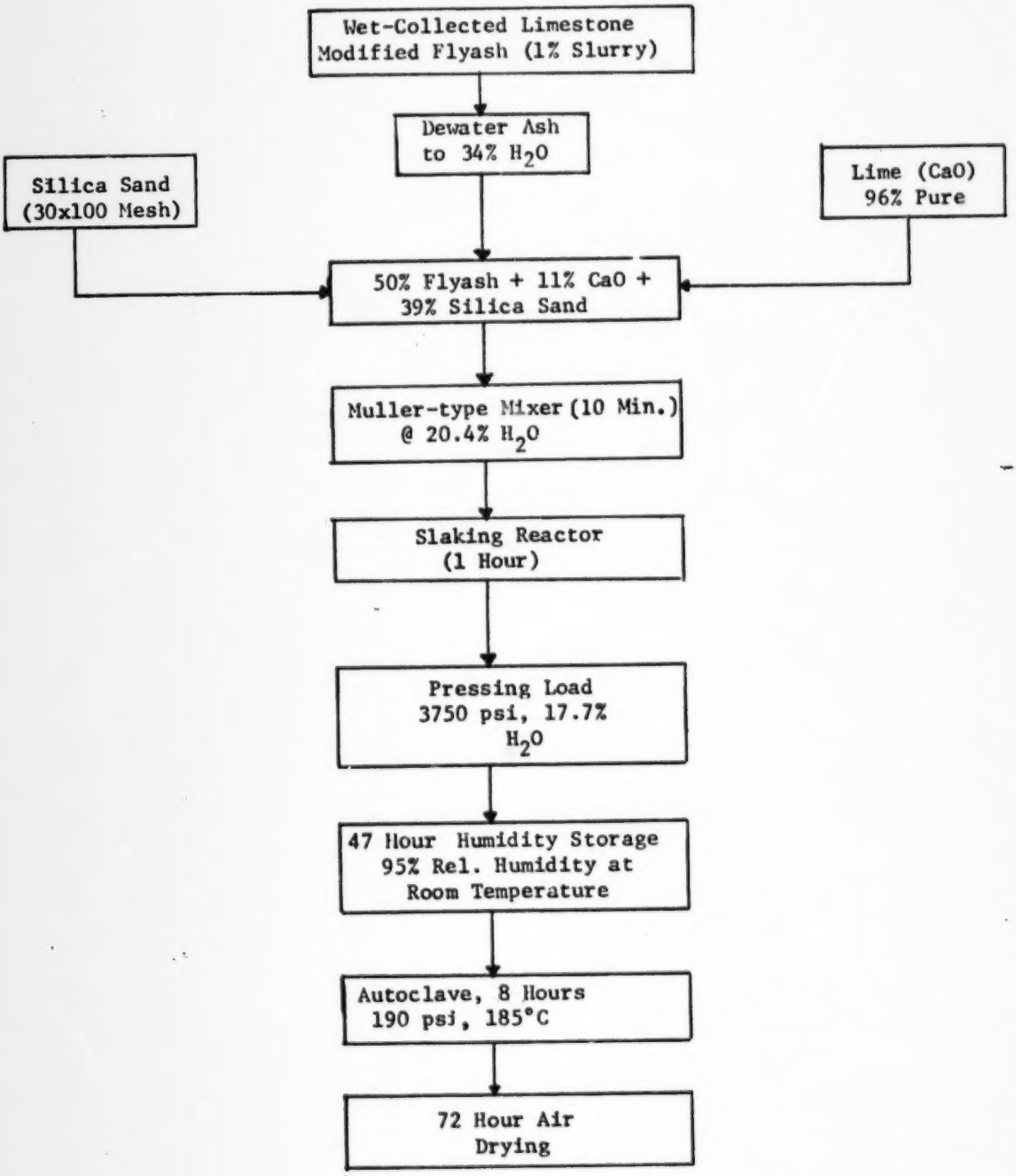
Under the subject contract, structural shapes were produced using, on a dry basis, 100 percent wet-collected, limestone-modified ash. A flowsheet of the process, Figure 5, which yielded the maximum compressive strength is included. Samples produced using this method ranged in compressive strength between 875 psi and 960 psi. The blocks had a green strength before curing of approximately 400 psi and could withstand normal handling

TABLE 9

	Autoclave	Na Ion g/liter	Leach Time hours	Liquor Composition	Slurry Concentration g/l	Al Extraction Efficiency %
1	No	16	1/2	NaOH	10	20.2
2	Yes	16	1/2	NaOH	10	22.4
3	No	41	1/2	NaOH	10	26.9
4	Yes	41	1/2	NaOH	10	30.3
5	No	16	2	NaOH	10	31.4
6	Yes	16	2	NaOH	10	26.9
7	No	41	2	NaOH	10	30.3
8	Yes	41	2	NaOH	10	36.0
9	No	35.7	1/2	NaOH, Na_2CO_3	10	----(1)
10	No	35.7	1/2	NaOH, Na_2CO_3	100	12.7
11	No	35.7	1	NaOH, Na_2CO_3	10	43.8
12	No	35.7	1	NaOH, Na_2CO_3	100	13.4
13	Yes	35.7	1/2	NaOH, Na_2CO_3	10	37.0
14	Yes	35.7	1/2	NaOH, Na_2CO_3	100	3.8
15	Yes	35.7	1	NaOH, Na_2CO_3	10	44.9
16	Yes	35.7	1	NaOH, Na_2CO_3	100	10.8
17	Yes	35.7	1/2	NaOH, Na_2CO_3	10	17.5
18	No	35.7	1/2	NaOH, Na_2CO_3	10	33.4
19	Yes	35.7	1	NaOH, Na_2CO_3	10	18.5
20	No	35.7	1	NaOH, Na_2CO_3	10	47.1
21	Yes	39.7	1/2	9NaOH, 1Na_2CO_3	10	12.5
22	No	39.7	1/2	9NaOH, 1Na_2CO_3	10	32.3
23	Yes	39.7	1	9NaOH, 1Na_2CO_3	10	11.0
24	No	39.7	1	9NaOH, 1Na_2CO_3	10	36.1
25	Yes	35.7	2	NaOH, Na_2CO_3	20	37.0
26	Yes	38.4	2	3NaOH, 1Na_2CO_3	10	43.7
27	Yes	38.4	2	3NaOH, 1Na_2CO_3	20	37.6
28	Yes	41	4	NaOH	10	37.9
29	Yes	41	2	NaOH	10	37.0
30	No	41	2	NaOH	10	32.5
31	Yes	85.9	2	NaOH	10	30.3
32	Yes	41	2	NaOH	20	26.4
33	Yes	41	2	NaOH	20	27.5
34	Yes	41	1	NaOH	20	25.2
35	Yes	41	2	NaOH	20	29.5
36	Yes	41	1	NaOH	100	9.0
37	Yes	41	1/2	NaOH	20	3.9
38	Yes	41	1/2	NaOH	100	8.87
39	Yes	41	24	NaOH	20	17.1
40	Yes	H_2O	48	----	100	0.02
41	Yes	41	48	NaOH	100	1.95
42	Yes	41	12	NaOH	100	4.97
43	Yes	85.9	24	NaOH	50	4.20
44	Yes	85.9	48	NaOH	100	1.14
45	Yes	75.4	24	NaOH, Na_2CO_3	100	0.54
46	Yes	112	24	4NaOH, 1Na_2CO_3	50	3.82
47	Yes	41	24	NaOH	100	8.42
48	Yes	41	48	NaOH	100	3.91
49	Yes	85.9	24	NaOH	100	3.19
50	Yes	80.6	24	3NaOH, 1Na_2CO_3	100	3.1
51	Yes	58.4	24	2NaOH, 1Na_2CO_3	100	1.78

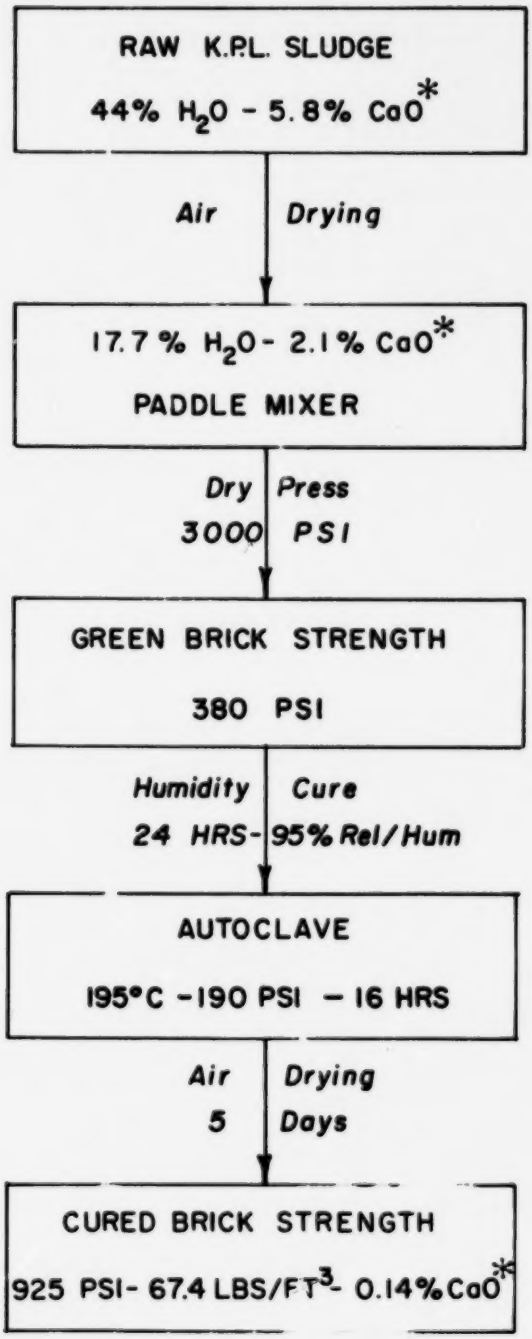
(1) Sample contaminated - test not rerun

Figure 4


Wet-Collected Limestone Modified Flyash (1% Slurry)
Dewater Ash to 34% H_2O
Silica Sand (30x100 Mesh)
Lime (CaO) 96% Pure
50% Flyash + 11% CaO + 39% Silica Sand
Muller-type Mixer (10 Min.) @ 20.4% H_2O
Slaking Reactor (1 Hour)
Pressing Load 3750 psi, 17.7% H_2O
47 Hour Humidity Storage 95% Rel. Humidity at Room Temperature
Autoclave, 8 Hours 190 psi, 185°C
72 Hour Air Drying

Flow Sheet: Optimum Conditions for the Production of Calcium-Silicate Brick from Wet-Collected Modified Ash.

Figure 5



* "Free" or Reactive Lime Reported as CaO

FINAL FLOW CHART FOR THE PRODUCTION OF STRUCTURAL PRODUCTS FROM 100% WET-COLLECTED LIMESTONE MODIFIED FLYASH

procedures. The low final strength, approximately 3600 psi lower than those required by ASTM specifications, prompted a further study to determine whether all of the calcium constituents were being utilized during autoclaving. The study showed that the modified ash examined had 5.8 percent "free-lime" or reactive lime present before processing and that only 0.14 percent remained after curing. This data indicates that almost all of the "free-lime" originally available was chemically combined during processing and that very little increase in compressive strength could be obtained.

Conclusions. Although very satisfactory calcium-silicate products can be produced using modified flyash, sand and lime, the use of 100 percent wet-collected modified ash does not appear feasible. The maximum compressive strength obtained was less than 1000 psi although "free-lime" tests indicated that almost all of the reactive calcium was chemically combined during processing.

ALUMINUM EXTRACTION

A bench-scale extraction program designed to investigate the potential recovery of aluminum values present in KPL wet-collected, limestone-modified flyash was performed. The basic approach taken considered the modified ash as being similar in nature to the materials produced using conventional lime-sintering processes. The basis for such an approach lies in the direct similarities between the mode of formation and the initial compounds present in lime-sintering processes and modified ash. Lime-sintering involves the mixing of alumino-silicates, eg, clay or flyash, with lime and then roasting to form calcium aluminates and insoluble dicalcium silicates. It was hoped that the presence of excess lime during the coal combustion process would allow the formation of sinter products. Extraction performed using sodium hydroxide, sodium carbonate, or a mixture of these as solvents for the

calcium aluminates showed that less than one half of the aluminum present in the modified ash could be extracted. It was assumed that the sintering process did not go to completion due to the relatively short contact time between the lime and the coal ash materials in the boiler. Potential sintering time in the boiler flame envelope would generally be measurable in seconds or fractions of seconds compared to a normal sintering time of one half hour or more. In addition, a portion of the calcium present is used up in sulfur oxide capture. A further sintering step might provide the desirable calcium aluminates; however, such a process would re-release the sulfur components in gaseous form.

Autoclaving was examined as a means of further solubilizing the aluminum containing constituents of the modified ash. The variables which were monitored included: solvent type, solvent concentration, contact time, solid-to-liquid ratio, and such autoclaving factors as temperature, pressure, and duration.

A. Literature Studies. Currently, less than ten percent of the aluminum produced in the U. S. is derived from domestic ores and the increasing use and strategic importance of this metal has led to a re-examination of locally available materials such as kaolin, other aluminum bearing clays, ferrugineous bauxite and anorthosite as potential ores for the near future. In an effort to determine the types of reactions involved in the processing of such ores, a partial technical discussion and literature survey was prepared (see Appendix C). In addition, discussions were held with personnel of the College Park, Maryland, Station of the U. S. Bureau of Mines who are currently investigating the recovery of aluminum from unmodified coal flyash.

B. Experimental Methods and Results. Extraction tests were performed using sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and combinations of the two in varying leach liquor concentrations, slurry concentrations and contact durations. The criterion chosen as a basis for comparison between tests was the extraction efficiency (amount of aluminum in leach liquor/total amount of aluminum available in the sample). In order to obtain the maximum information possible from a limited number of experiments, all test series were systematically planned following established factorial design methods. All samples were leached in glass beakers at 95 to 100°C and agitation was supplied by Teflon coated magnetic stirring bars.

1. Autoclaving - The conditions within the autoclave for the majority of the tests were 190 ± 5 psig of steam pressure at 188 ± 3°C for 24 hours. This temperature and resultant pressure were selected as they are easily reached and monitored by most commercial autoclaves. Figure 6 illustrates graphically the effect of autoclaving upon aluminum extraction efficiency using paired tests in which autoclaving is the only variable within each pair. A listing of the conditions for each numbered test may be found in Table 9. As can be seen from the figure, autoclaving did not significantly increase the extraction efficiency in any test pair and in four of the test pairs significantly depressed the efficiency. These four test pairs were all leached with a combination of NaOH and Na_2CO_3. The autoclaving time of 24 hours was selected for the tests because structural material testing had indicated that almost all of the autoclaving reactions went to completion within 12 to 18 hours. It is possible that higher steam temperature and pressure combinations might improve the extraction efficiency, but the costs in equipment and energy requirements of such a program would probably preclude any industrial acceptance.

2. Leach Contact Time - The effect of increasing leach solution-modified ash contact time upon the extraction of aluminum is shown graphically in Figure 7. As the contact time increased from 1/2 to four hours, the extraction efficiency generally increased. As can be noted from the figure, the amount of increase for a set of specific test conditions would not be predictable for a given time increase; and specific process tests would have to be performed before a relative increase could be calculated. No tests were performed to accurately determine an optimum contact time for each set of test conditions; however, it was noted that the percentage of available

Figure 6

THE EFFECT OF AUTOCLAVING UPON ALUMINUM EXTRACTION EFFECIENCY

PAIRED TESTS DIFFER ONLY IN AUTOCLAVING AND THE DIFFERENCE BETWEEN SETS OF TESTS IS SHOWN IN TABLE 9.

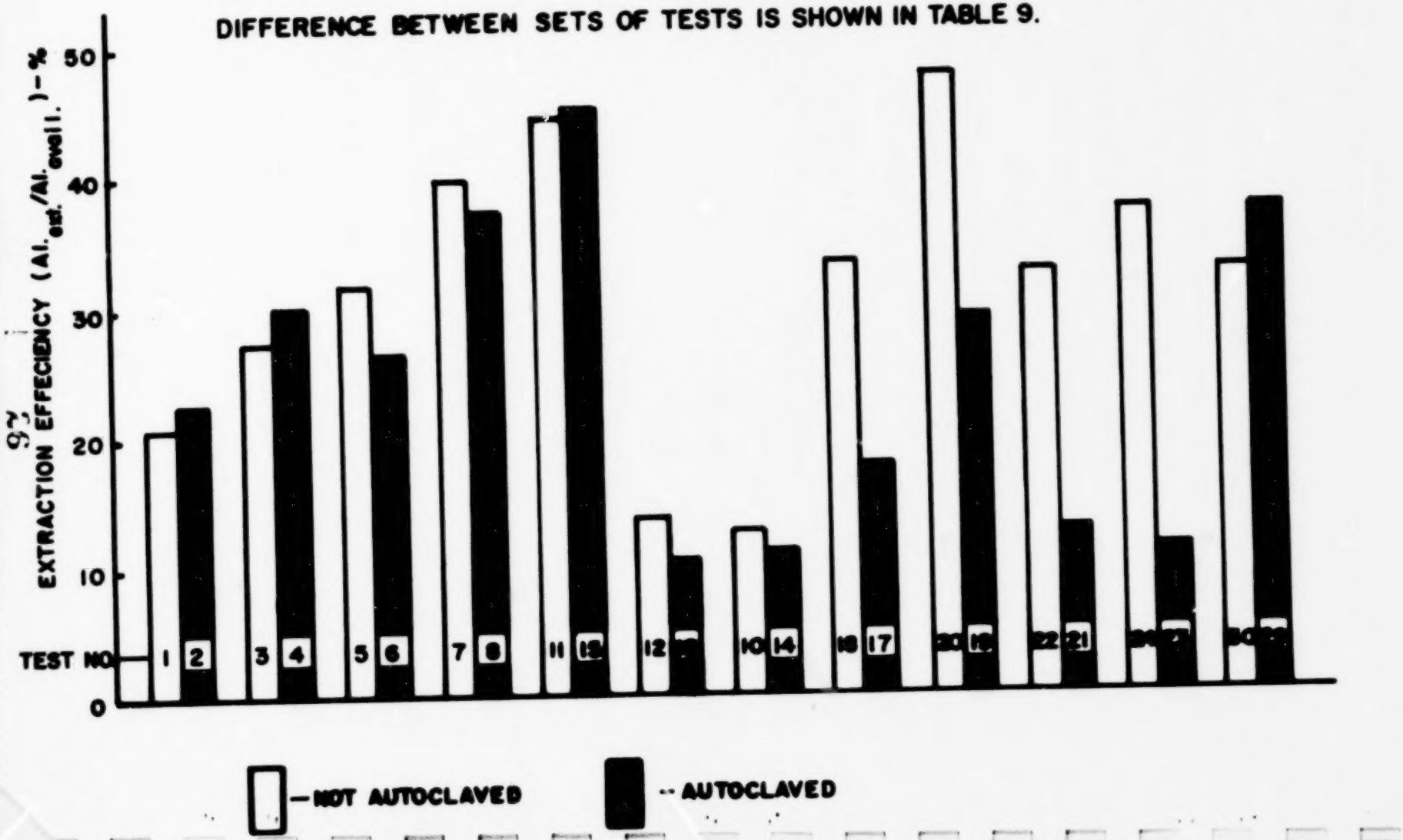
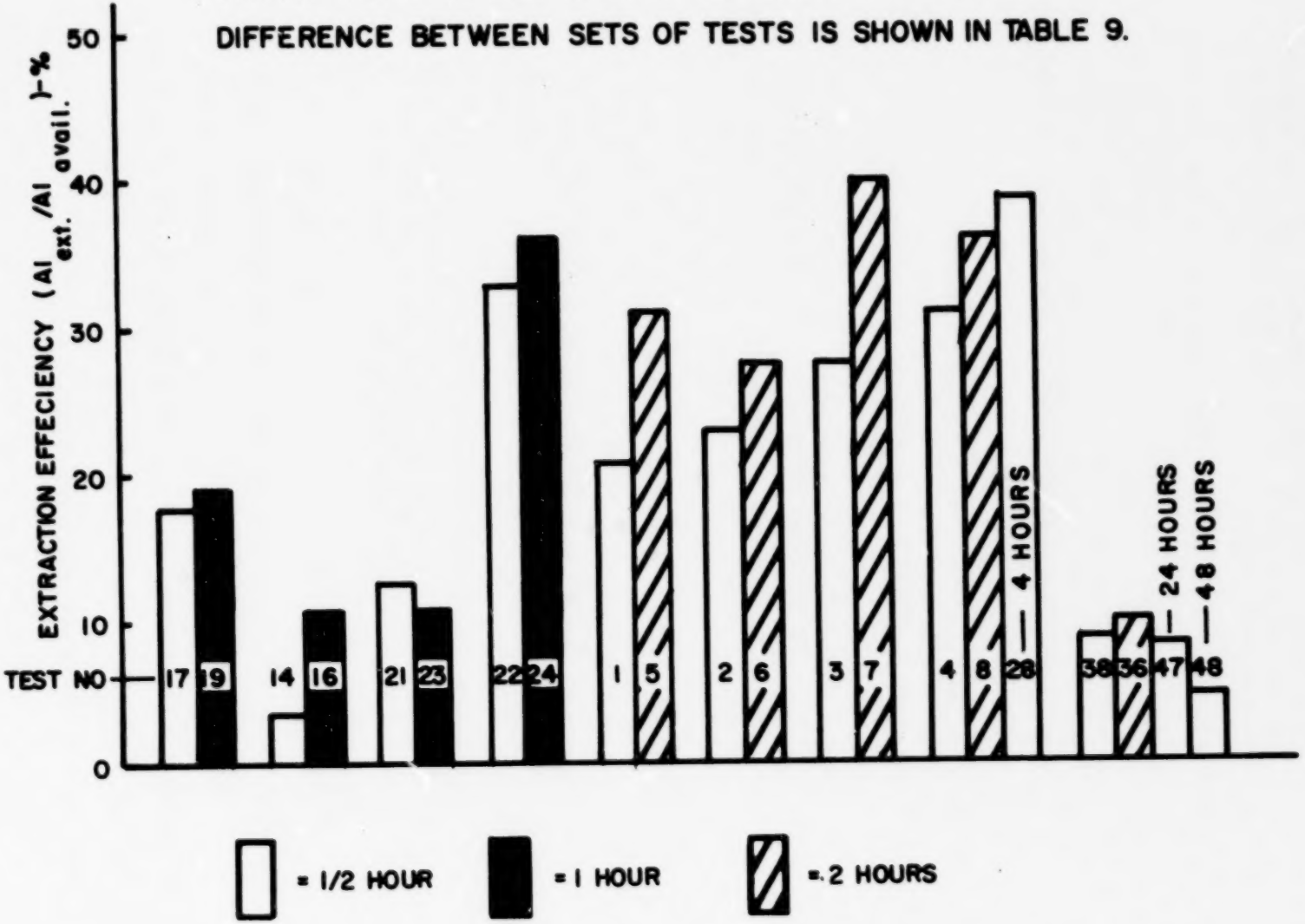


Figure 7

THE EFFECT OF LEACHING TIME UPON ALUMINUM EXTRACTION EFFECIENCY

PAIRED TESTS DIFFER ONLY IN LEACHING TIME AND THE DIFFERENCE BETWEEN SETS OF TESTS IS SHOWN IN TABLE 9.



aluminum extracted lowered as the contact time increased past 24 hours. Such an effect could have been caused by the formation and precipitation of hydrated calcium aluminates from the leach liquor.

3. Sodium Ion Concentration - The aluminum extraction efficiency was also related to the sodium concentration (Na g/liter) available to the leach liquor. As shown in Figure 8, an increase in Na concentration from 16 to 41 g/liter led to a 20 to 30 percent increase in extraction efficiency. However, a further increase in Na concentration to 85.9 g/liter led to decreased efficiency. Further optimization tests were not performed.

4. Slurry Concentration - Slurry concentration, expressed as grams of flyash per liter of leach liquor, had the most definite effect on extraction of the variables monitored. As shown in Figure 9, a decrease in the solids content of the leach slurry led to an increase in the percentage of aluminum extracted. Such a relationship is to be expected as extraction is partially dependent upon the number of solvent ions which contact the aluminum present and also upon the availability of water for solution. No tests were performed to determine an optimum slurry concentration due to the large number of other related variables.

5. Physical Factors - The most important physical characteristic of limestone modified flyash, as related to extraction of aluminum, is its particle size. By weight, greater than 95 percent will pass through a 74 micron sieve and approximately 85 percent will pass through a 38 micron sieve. An advantage of the extremely fine particle size lies in the resultant extremely large surface area per unit weight of the flyash which allows a large contact area between leach liquor and particles. However, this large surface area also makes release and recovery of the leach liquor after extraction very difficult as the leach liquor tends to adhere to the particles and is very difficult to filter or wash off the very fine material.

The glassy nature of the flyash is also an important factor in that the aluminum present is probably derived from coal-associated shales and clays. Fusing of these silicates during combustion probably further incorporates a large amount of the aluminum present within the silicate structure. Therefore, complete recovery of the metal would require a complete dissolution of the glassy siliceous matrix.

Figure 8

THE EFFECT OF SODIUM ION CONCENTRATION UPON ALUMINUM EXTRACTION EFFECIENCY

PAIRED TESTS DIFFER ONLY IN Na^+ ION CONCENTRATION AND THE DIFFERENCE BETWEEN SETS OF TESTS IS SHOWN IN TABLE 9.

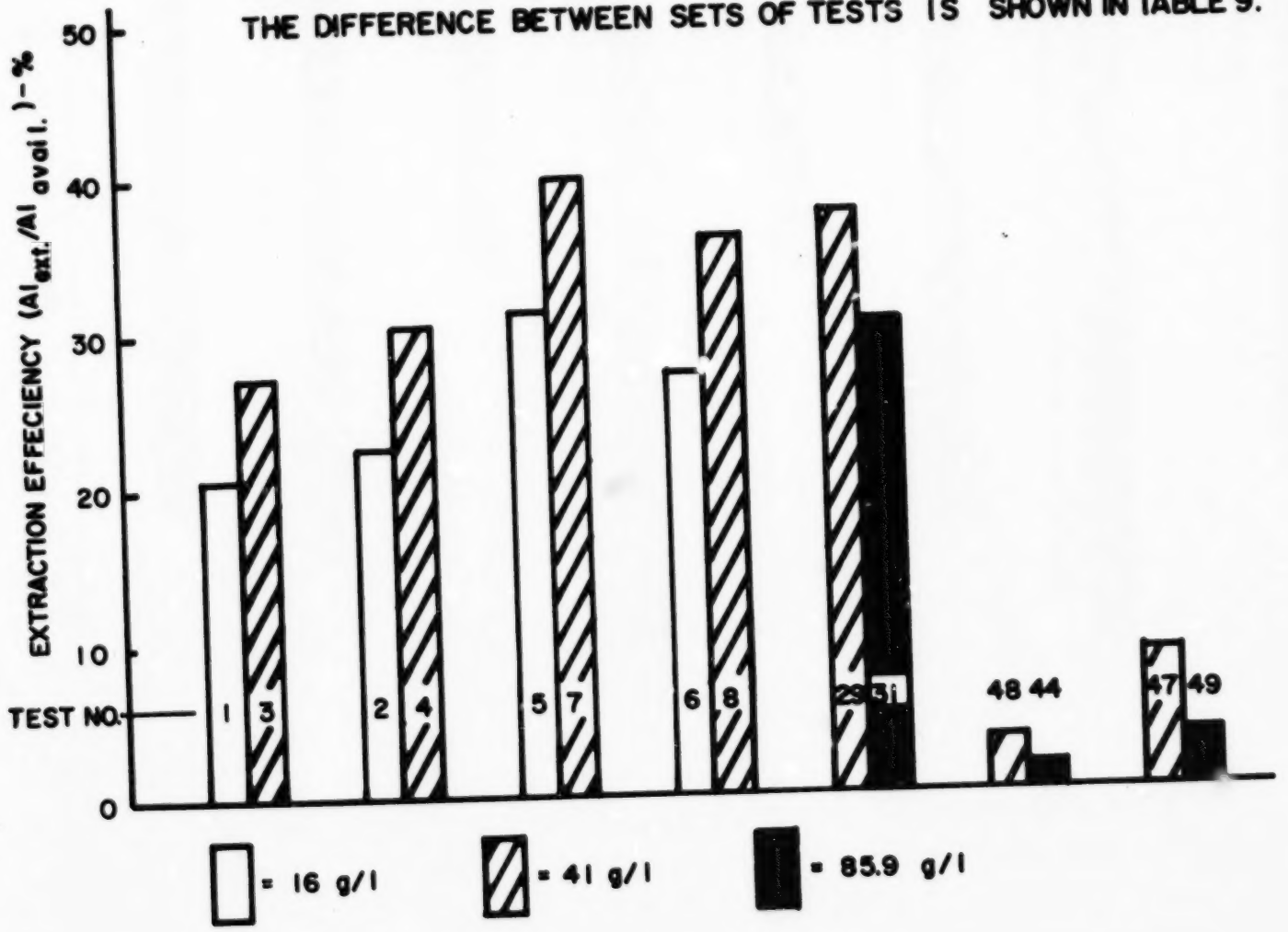
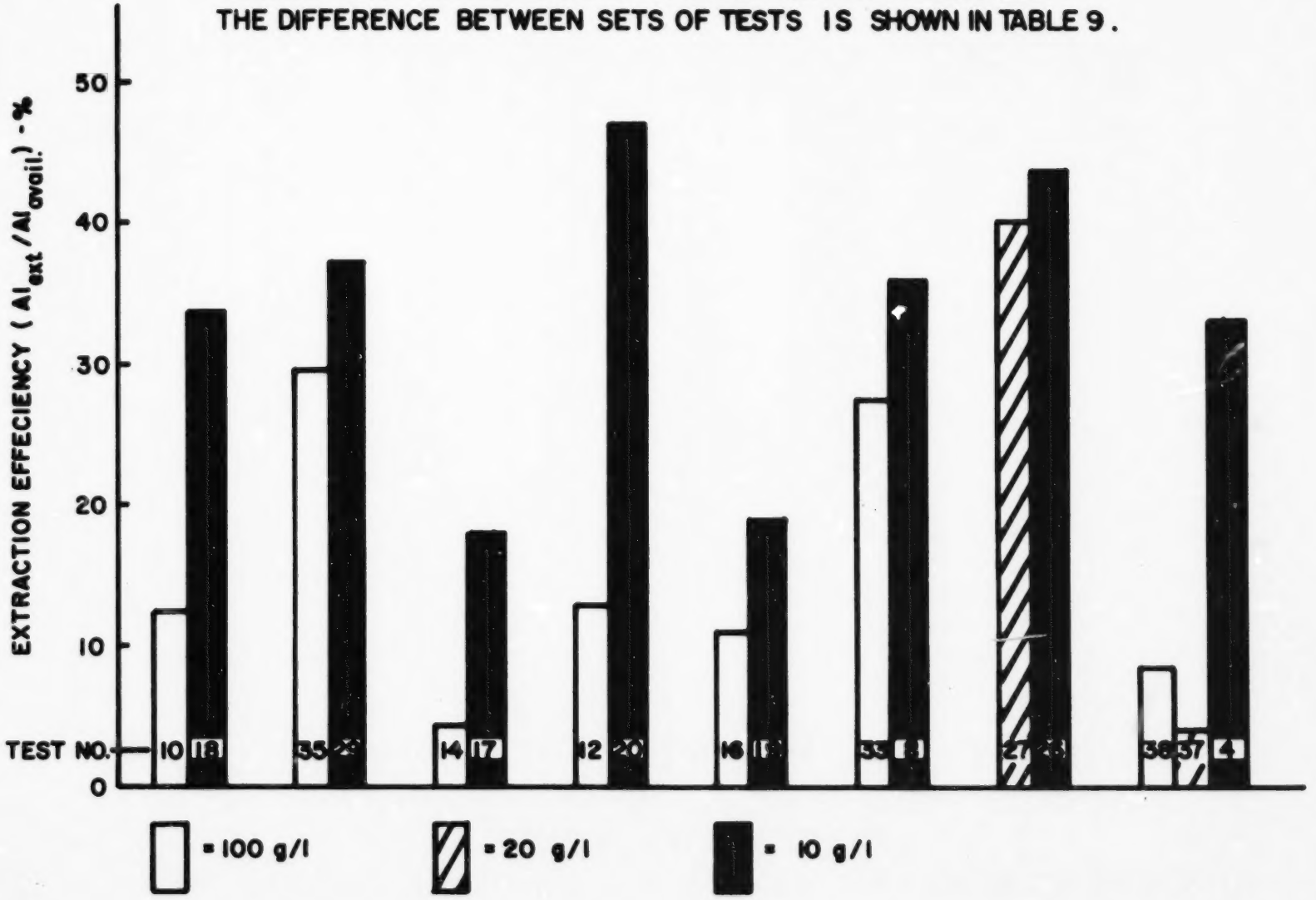


Figure 9

THE EFFECT OF SLURRY CONCENTRATION UPON ALUMINUM EXTRACTION EFFECIENCY

PAIRED TESTS DIFFER ONLY IN SLURRY CONCENTRATION AND THE DIFFERENCE BETWEEN SETS OF TESTS IS SHOWN IN TABLE 9.



C. Conclusions. Recovery of aluminum from wet-collected, limestone-modified flyash by methods similar to those employed in lime-sintering processes is a highly complex process made more difficult by the extremely fine particle size and low aluminum content of the ash. Inter-relationships were found between all of the process variables monitored and the aluminum extraction efficiency. In effect, a very close monitoring of all aspects would have to be performed to achieve maximum extraction. In addition, sufficient contact time is not available during combustion to completely convert the aluminum present into the desired calcium aluminates; but further sintering is probably inadvisable due to the re-release of the trapped sulfur gases. Autoclaving of the ash, although it did not re-release the sulfur, was considered unsuccessful as a method of forming the desired calcium aluminates.

APPENDIX A

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INTRODUCTION

Dewatering is defined as the separation of a mixture of solids and water into two parts, one of which is relatively solid free, and the other relatively liquid free.[1]

Such a process requires that the forces binding the liquid to the solid be overcome.

These forces include:

1. Physical and chemical forces which directly bind the liquid to the solid.
2. External forces such as gravity, electrical fields, and thermal energy which bind the liquid and the solid.
3. Properties of resistance in flowing fluids and media.

The problem of solid-liquid separation is one which occurs in practically every industry. The sludges from industry may create a health problem or they may contain materials which are of value economically. Thus, it is essential that efficient, inexpensive methods of dewatering sludge be available.

The practice of utilizing materials from waste water is not new.[2] As early as 1740, the French were extracting chemicals from waste waters. In 1884, the English first used filter presses to dewater waste sludges. Between 1880-1900, the use of chemicals and filtration in treating wastes became established in the United States.

DEWATERING METHODS

The major methods of dewatering are gravity thickening, vacuum filtration, and centrifugation. Other methods which find limited utilization include:

electrophoresis, vibration sieving, filter pressing, pressure filters, precoat filters and hot air drying.

Gravity Thickening:

Concentration can be affected by allowing the sludge to settle with or without stirring or chemical conditioning. The cheapest and simplest means of dewatering is gravity thickening. In this technique the solids are allowed to settle out of suspension under the influence of gravity. The success of this method is dependent upon the nature of the solids, their ability to form flocs (combination of small solid particles into larger ones), the degree of compaction (final settled sludge volume) and the ease of elimination of water from the settling material. The sludge concentrate should be gently stirred so as to break down structures which have formed during sedimentation.

There are several advantages to thickening before further treatment. These include:[3]

(a) reduction of sludge volume

(b) reduction of conditioning cost (ie, addition of chemical conditioners)

(c) reduction of water content and

(d) reduction of over-all treatment cost (ie, secondary treatment processes).

The thickened sludge is compacted and a great deal of the water is removed but interstitial water is still present and is not easily removed. Thus, further treatment is often required.

Vacuum Filtration:

Vacuum filtration of process industry slurries has been practiced for many years. Since 1960, the use of vacuum filtration has risen for the following reasons:[4]

(a) development of self-cleaning media such as polyfilament fibers,

(b) increased cost of alternate methods and

(c) applicability to all sewage wastes and to many industrial wastes.

In vacuum filtration a rotary drum passes through a slurry tank and solids are retained on the drum surface under vacuum.[5] As the drum rotates through the slurry, a cake is built up and the water is removed by vacuum. The emerged solids are dewatered under vacuum and then are removed from the drum, generally by scraping at the end of each cycle. There are several advantages to vacuum filtration which include:

(a) variety of sludges dewatered,

(b) low floor space requirement,

(c) relatively dry filter cake produced, and

(d) good solids capture.

These advantages are somewhat offset by possible disadvantages which include:

(a) frequent blinding (clogging of pore spaces by fine particles) of filter media,

(b) operators required, and

(c) lack of precise scientific control.

In choosing the filter media to be used, several factors must be considered.[6] If the filter medium is a cloth fabric, the individual fibers may embed in the filter cake causing the cake to adhere to the drum. The filter medium must be strong enough to withstand the strain created by the vacuum without rupturing. Also, the pore size should be such that the fine solids are retained but blinding is kept at a minimum. The materials which are commonly used include: cotton, synthetic fibers, metallic cloths, and punched rubber sheeting. Cotton cloth is usually used in milling since it has the advantages of great tensile strength, flexibility, durability, and is easily cleaned.

Chemical conditioning of the slurry to enhance the efficiency of dewatering is often a necessary step before sludge vacuum filtration.

Pressure Filtration:

Pressure filtration has been found to be effective in dewatering and is simple, flexible and can be used either with or without chemical reagents.

The pressure from the slurry pump is adequate for dewatering the slurry in most cases.

There are several variables which need to be considered in relationship to each specific sludge.

Process Variables:

(a) feed rate or slurry concentration

(b) feed consistency

(c) particle size

Machine Variables:

(a) capacity of filter cake area

(b) amount of time required to remove filter cake and replace filter on stream

Miscellaneous Methods:

There are many other methods which may be used to affect sludge dewatering. Briefly, they include:[7]

(a) Electrophoretic dewatering in which the particles migrate in an electric field to a point of concentration or collection;

(b) Vibrational sieving, used with coarse suspensions;

(c) Filter presses which may be used for sludges which are rich in minerals and may be desiccated without previous treatment;

(d) Centrifugation which can normally be used with nonabrasive slurries;

(e) Precoat filters which involve an auxiliary layer of diatomaceous earth, sawdust, or an ash covering a membrane filter. The need

for prior conditioning is generally eliminated by precoating the filter; and

(f) Drying by hot air, drying drum, rotary dryer, pressure drying multistage drying, or thermal spray drying.

DEWATERING AIDS

In many instances sludges can be dewatered by various combinations of the above methods to yield a product of proper moisture content for utilization or disposal. However, in numerous other slurries, including wet collected modified flyash, the particles are of such minute dimensions that they settle out of suspension very slowly and can pass through ordinary filters. These materials may require the use of inorganic chemical conditioners to coagulate or organic chemical conditioners to flocculate the fine particles prior to dewatering by the above methods.

Coagulation:

The stability of fine particles that resist coagulation is a result of electrostatic forces and hydration which involve the charging of surface components and the subsequent adsorption of ions from solution.

The influence of charge on the stability of dispersed systems of particles is a function of the zeta potential, which is the magnitude of the potential difference of the boundry between the volume of liquid held by the particle and the solution.[8]

The value of the zeta potential in millivolts (mv) may be determined by use of a zeta meter.

The stability of a colloidal system decreases as the zeta potential of the component particles approach a value of zero mv.[9]

The coagulation of dispersed particles (particles that have zeta potentials greater than $\pm$ 15 millivolts) by charge reduction is often induced by the addition of chemical electrolytes which reduce the electrostatic forces.

The slurry is generally agitated to insure collision between particles.

With inorganic electrolytes the coagulation power of bi-valent ions is about 20 to 80 times greater than that of uni-valent ions and the coagulation power of tri-valent ions is many times greater than that of bi-valent ions.[10]

As a rule, the higher the charge of an ion the smaller its solvated volume rendering it more useful in charge reduction.[11] Thus, hydrolyzed tri-valent metal salts such as $Al_2(SO_4)_3$, $Al(NO_3)_3$ and $Fe_2(SO_4)_3$ have been investigated as coagulants for lyophobic sols.[12] The results of these experiments indicate that aging of the salt solution has a strong effect on the coagulation of the sol. In all cases studied using $Al_2(SO_4)_3$, aging was found to reduce the critical coagulation concentration (C.C.C.). When a common ion (K_2SO_4) was added, the C.C.C. was observed to decrease slightly.

Flocculation:

Observations of flocculation phenomena have led to the formulation of three possible mechanisms of flocculation.[13]

1. Charge Effect Neutralization: The net effect of the electrostatic repulsive forces is neutralized between particles having a double layer. The polyelectrolytes compress the double layer allowing the attractive forces to act.

2. Polymer Bridging: The process involves the use of a flocculant to interfere with the free movement of sol particles. This may occur as a result of the adsorption of a number of particles on the polymer network or the formation of a bridge between two particles which would not readily interact.

3. Mutual Dehydration: A non-ionic flocculant reacts with a sol to form an insoluble precipitate.

Starch was the first long chained molecule used as a flocculant.[14] Other natural products which have been used include: locust bean gum, cactus extract, linseed, glue, gelatin, etc.

Gelatin has been thought to be unique in that it is applicable to any suspension under the appropriate conditions.[15] Flocculation with gelatin

is also pH dependent and the best results are obtained under conditions where the gelatin carries a small positive change.[16]

Since the early 1950's, a wide variety of synthetic polymers have become available for use as flocculants.

In order to be effective, a flocculant must have certain characteristics.[17]

1. The molecules must contain polar groups such as -COOH or -OH which can be adsorbed on the particle surface.

2. The molecule must be of sufficient length to form a bridge between particles producing uniform flocs of a proper size and shape to give the filter cake the proper porosity.

3. The flocculant must be water soluble and the effective concentration must be very small.

4. The molecules should have a good scavenging and binding ability in order to gather up the sol particles and resist deformation of the filter cake under vacuum filtration.

Healy and LeMer[18] have developed a quantitative theory of flocculation in which the optimum flocculation occurs with 50 percent of the surface being covered with polymers. When the amount of surface covered reaches 100 percent, the flocs become metastable and may re-disperse due to the insulative effects of excess flocculant.

Molecular weight of the polymer is important in the flocculation process. Flocculation is improved by using polymers of high molecular weight, but too high a molecular weight will cause fast settling of the floc leaving fines in suspension.[19]

Non-ionic polymers have been studied as flocculating agents for dilute clay suspensions.[20] It was found that polyethylene oxide will be absorbed on clay sols and form a floc by a bridging mechanism. The process is pH dependent and also is dependent upon the counter ions present.

Studies of the flocculation of silica suspensions by cationic polymers indicate that flocculation can occur with polymers of low molecular weight.[21] Much interest has developed in these cationic polymers. Polyacrylamide has been investigated as a flocculate for the mining industry.[22] It has been found to be remarkably versatile. Suspended solids from sewage, coal mines, and chemical precipitates have been studied.

Thus, it would appear that the use of flocculants or coagulants is the best approach for removing fines from suspension. The concentrations of the conditioners involved are small enough that, for most processes, the additional electrolytes would not present a water purity problem. With polymers, heating to an elevated temperature should remove the organic materials as oxidized products. Polymeric flocculation will increase the water content of the floc over that of an untreated floc.

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APPENDIX B

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FLOCCULANT FILTERABILITY TESTING

These techniques include the Buchner funnel test, the vacuum break test, and the filter leaf test, and constitute a laboratory testing program to provide information on optimum additive concentration and specific vacuum filter cycle segments. Using this information, a slurry dewatering program can be designed.

A. Buchner Funnel Test:

The Buchner funnel test is a common method by which optimum flocculant concentration may be obtained.

Procedure: Flocculant solutions are prepared by dissolving 0.1 gram of flocculant in 99.9 ml of water to form a stock solution. 12.5 ml of the stock solution is then diluted to 500 ml for use in the flocculation studies.

Samples are prepared for filtration by mixing 100 ml of concentrated slurry with flocculant and distilled water in the proportions presented in Table 1.

TABLE 1

mls of Flocculant	mls of Water	Sample Total Vol.	(ppm) Floc. Conc.
0.0	30.0	130 ml	0.000
0.5	29.5	"	0.096
1.0	29.0	"	0.193
2.0	28.0	"	0.386
3.0	27.0	"	0.579
5.0	25.0	"	0.965
10.0	20.0	"	1.930
15.0	15.0	"	2.895
20.0	10.0	"	3.860
25.0	5.0	"	4.825
30.0	0.0	"	5.790

The samples are then vacuum filtered under 5 inches of mercury vacuum and the filtrate volume is recorded at the end of 0.5 minutes. The optimum flocculant concentration is selected on the basis of maximum filtrate volume and clarity.

B. Filter Break Test:

The filter break test is an extension or refinement of the Buchner funnel test. A flocculated sample of sludge is filtered until it reaches dryness. Air then enters the system through drying cracks or breaks and the vacuum decreases. The time required until the vacuum drops is recorded.

Procedure: The optimum amount of flocculant determined in the Buchner funnel test is completely mixed with a 100 ml sample of sludge. The flocculated sludge is then filtered under a vacuum of 10 inches Hg and the time required for the vacuum break to occur is determined. At this point the vacuum would no longer be effective as air would be passing through the cake.

C. Filter Leaf Test

The filter leaf test is designed to reproduce the operating cycle of a commercial vacuum filter.

Procedure: A series of filter media to be examined along with a filter leaf apparatus having a leaf area of 0.1 ft^2 are used.

The optimum flocculant concentration determined from Buchner funnel tests is added to 900 ml of slurry. The filter leaf with attached cloth is submerged in the flocculated slurry and a vacuum of 15 inches Hg is applied to the system for 1.5 minutes. The leaf is then removed from the slurry and held upright for three minutes. The percent moisture, thickness of the filter cake, and the volume of filtrate are recorded. The resultant information can then be used in the design of a field size vacuum filter dewatering operation by using scale-up factors determined by specific equipment manufacturers.

APPENDIX C

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ALUMINA LEACHING

When World War II began, the United States Government realized the seriousness of the situation that could arise if the existing supply of bauxite were cut off. Since then, extensive studies have been made of methods to extract alumina from clays and other alumina-silicates. The methods to be discussed in this summary include sinter processes, acid processes, and alum processes.

Sintering Processes:

Two general approaches have been taken in sintering processes. These methods are generally referred to as the lime sinter and the lime-soda sinter processes.

The lime sintering process is based upon reactions which convert aluminum silicates to calcium orthosilicates and calcium aluminates.

In the lime-sinter process, alumina bearing materials are mixed with limestone and are sintered to form calcium aluminate ($2CaO \cdot SiO_2$) from which the alumina is extracted as sodium aluminate ($NaAlO_2$) by leaching with NaOH, Na_2CO_3 or mixtures of these.(1)

$$3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + 17CaCO_3 \xrightarrow{1370°C} 5CaO \cdot 3Al_2O_3 + 6(2CaO \cdot SiO_2) + 17CO_2 + 6H_2O. \quad (1)$$

The calcium orthosilicate formed by the lime sinter process ties up nearly all of the silica present in a form which is insoluble in the leach liquor. As the sinter cools below 675°C, it undergoes a crystallographic change with a subsequent increase in volume resulting in powdering or "dusting" of the sinter. This provides a much greater surface area and the alumina becomes more accessible to the leach liquor.

Lundquist and Leitch(2) have investigated the solubility of monocalcium aluminate in water, sodium hydroxide, sodium carbonate, and mixtures of these.

They reported that calcium aluminate exibited a very limited solubility (11g/liter) in water even though it was completely hydrolyzed.

Soluble alumina did appear in solution, probably due to the presence of $(OH)^-$ from the $Ca(OH)_2$ generated during the hydrolysis reaction. The end result of the hydrolysis was represented by:

$$3[CaO \cdot Al_2O_3] + 12H_2O = Ca_3[Al(OH)_6]_2 + 4Al(OH)_3$$

The maximum soluble alumina concentration occurred within the first hour. The temperature of the leaching tests had a negligible influence on the initial extraction of soluble alumina, moderate effect on the precipitation of $Al(OH)_3$ and a strong influence on the crystal structure of hydrated calcium aluminates formed.

The solubility of $CaO \cdot Al_2O_3$ in NaOH was observed to be similar to its solubility in water. The reaction with NaOH may be represented by:

$$3[CaO \cdot Al_2O_3] + 4NaOH + 12H_2O \quad Ca_3[Al(OH)_6]_2 + 4Na^+ + 4Al(OH)_4^-. \tag{3}$$

The presence of NaOH provides additional $(OH)^-$ ions to inhibit the precipitation of $Al(OH)_3$.

The amount of $Al(OH)_3$ precipitated or dissolved is dependent upon the following reaction:

$$Al(OH)_3 + (OH)^- \quad Al(OH)_4^-. \tag{4}$$

The amount of $(OH)^-$ in solution available during the reaction depends upon the composition of the leach liquor, the extent of hydrolysis, and the amount of calcium aluminate initially in the material to be leached. The formation of soluble sodium aluminate is offset by the precipitation of hydrated calcium aluminates.

The reaction which occurs when sodium carbonate is used is:

$$CaO \cdot Al_2O_3 + Na_2CO_3 + 4H_2O \quad CaCO_3 + 2Na^+ + 2Al(OH)_4^-. \tag{5}$$

In this reaction, $CaCO_3$ becomes the principle precipitate instead of the less desirable insoluble $Ca_3[Al(OH)_6]$. Thus, a combining of carbonate, to prevent precipitation of the aluminates, and sufficient OH^- to hold alumina in solution should provide maximum alumina extraction.

The lime-soda process is not significantly different from the lime sinter process. Ground siliceous ore is mixed with limestone and sodium carbonate to give a mixture corresponding to dicalcium silicate and sodium aluminate.(2)

Peters and coworkers(3) have evaluated a lime-soda process for producing alumina from clay. The sintering reaction is represented by:

$$(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + 4CaCO_3 + Na_2CO_3 \quad Na_2O \cdot Al_2O_3 + 2H_2O + 2(2CaO \cdot SiO_2) + 5CO_2 \tag{6}$$

The temperature requirements, however, are not quite so high as they are in the lime sinter process. The dicalcium silicate doesn't undergo a phase change and "dusting." However, the sinter is usually less dense and is readily friable, porous and easily ground if it is not overburned.

Sodium aluminate is the principle aluminum compound formed in the lime-soda sinter process.

Lundquist and Leitch(4) have reported the solubility characteristics of sodium aluminate. They found that nearly all of the sodium aluminate added to H_2O, NaOH, or Na_2CO_3 dissolved. However, the resultant solution was unstable; the amount of aluminum in solution is dependent upon the amount of free OH^-. The early precipitation, however, of gibbsite is a

detrimental factor in the lime-soda process:

$$Al(OH)_4^- = Al(OH)_3 \text{ (Gibbsite)} + OH.^- \quad (7)$$

Thus, it is necessary that an excess of OH^- be present in order to prevent excess precipitation of gibbsite. Also, rapid removal of the tailing solids from the leach liquors aids in the inhibitation of gibbsite formation.

NATURE OF SODIUM ALUMINATE AND STRUCTURAL PHASES FORMED IN LIME-SINTER AND LIME-SODA SINTER PROCESSES.

Sodium Aluminate:

The dissolution of aluminum compounds in NaOH solutions takes place with the formation of sodium aluminate which is considered to be fully dissociated in solution.[5]

According to Pearson, the precipitation of aluminum hydroxide may be written:

$$Al(OH)_4 \cdot (H_2O)_2^- \qquad Al(OH)_3 + 2H_2O + OH^- \quad (8)$$

Lundquist[8] has suggested that the reaction is one of polymerization in the precipitation of an alumina gel or crystalline aluminum hydroxide. The initial polymerization reaction might be written:

$$2[Al(OH)_4 \cdot (H_2O)_2]^- = Al_2(OH)_8 \cdot (H_2O)_2^= + 2H_2O \quad (9)$$

The reaction builds longer ion units by addition of other monovalent ions. The growth of polyvalent ions continues through colloidal stages into the crystalline aluminum hydroxide.

Hydrated Calcium Aluminates Encountered in Lime-Sinter and Lime-Soda Sinter Processes:

The hydrated calcium aluminate $Ca_3[Al(OH)_6]_2$ is formed in the leaching step of both the lime-sinter and the lime-soda sinter processes. Also, in the lime-soda process the hydrate $3CaO \cdot Al_2O_3 \cdot (8\text{-}12)H_2O$ is formed.[9]

The hydrates which form may have very different crystallographic structures. The compound $3CaO \cdot Al_2O_3 \cdot (8\text{-}12)H_2O$ belongs to a group of compounds with the general formula of $nCa(OH)_2 \cdot nAL(OH)_3 \cdot pH_2O$ and forms hexagonal plates in a layered structure. The layers are thought to be built up of $Ca(OH)_2$ and $Al(OH)_3$ with variable water content between the layers.

The compound $Ca_3[Al(OH)_6]_2$ consists of compact cubic crystals with octahedral ions, $Al(OH)_6^{-3}$ held together by Ca^{++} in positions of eight fold coordination. It is ionic in nature and corresponds to a hydrogarnet mineral.

Nitric and Hydrochloric Acid Processes:

A. Nitric Acid Processes

Johnson and coworkers[10] have reported a nitric acid process for producing alumina from siliceous ores.

In this process, the clay is first calcined at 700°C and dehydrated to remove moisture and combined water. The aluminum is converted from insoluble aluminum silicates to an acid soluble compound upon dehydration.

$$(Al_2O_3 \cdot 2\,SiO_2 \cdot 2H_2O) \qquad (Al_2O_3 + 2SiO_2) + 2H_2O. \qquad (10)$$

A less than stoichiometric amount of 30% nitric acid is used to digest the clay at 165°C and 85 psig, thus forming a slightly basic aluminum nitrate solution in which iron is nearly insoluble,

$$(Al_2O_3 + 2SiO_2) + 6HNO_3 \qquad 2Al(NO_3)_3 + 2SiO_2 + 3H_2O. \qquad (11)$$

The iron and silica are removed by filtration. The aluminum nitrate solution is then concentrated by vacuum evaporation and aluminum nitrate nonahydrate is crystallized.

This hydrate is then fed to a fired rotary kiln operating at 500°C where the crystals decompose,

$$2[Al(NO_3)_3 \cdot 9H_2O \qquad Al_2O_3 + 3N_2O_5 + 18H_2O. \qquad (12)$$

The advantages of this method over other less expensive acid processes include: the lower solubility or iron in basic aluminum nitrate solutions, ease of decomposition of nitrates, simple recovery of acids. The disadvantages include: large cooling requirements, pressure digestion, comparatively expensive make up acid.

B. Hydrochloric Acid Processes

Peters and coworkers reported a series of hydrochloric acid processes for extraction of alumina.(11)

The major differences are found in the method of extraction of the alumina after leaching.

1. Isopropyl Ether Extraction

Calcined clay is leached with 20% HCl and the resulting slurry filtered to remove the silica residue,

$$(Al_2O_3 + 2SiO_2) + 6HCl \qquad 2AlCl_3 + 2SiO_2 + 3H_2O. \qquad (13)$$

Isopropyl ether is contacted with the leach liquor countercurrently and the iron removed through the formation of a complex:

$$[FeCl_3 \cdot HCl \cdot 10.3\,H_2O] \qquad x\,[(CH_3)4\,C_2H_2O]. \qquad (14)$$

The purified aluminum chloride solution is evaportated to form crystalline $[AlCl_3 \cdot 6H_2O]$.

The aluminum chloride is then decomposed at temperatures between 925-1100°C to yield aluminum,

$$2[AlCl_3 \cdot 6H_2O] \qquad Al_2O_3 + 6HCL + 3H_2O. \qquad (15)$$

2. Gas Precipitation Process

In this process calcined clay is digested with HCl and the slurry is filtered to remove silica residue. The filtrate is then treated with hydrogen chloride gas to precipitate $AlCl_3 \cdot 6H_2O$ leaving the iron in solution. The $AlCl_3 \cdot 6H_2O$ solution is then evaporated to form the hexahydrate which is then calcined to give alumina.

3. Gas Precipitation - Isopropyl Process

This is a modification of the previously described gas precipitation purification process. It has been studied because it offers a method by which iron precipitated with the aluminum chloride may be removed by extraction with isopropyl ether. Up to 95% of the iron contamination may be removed from the crude aluminum chloride by this method.

4. Caustic Purification Process

Calcined clay is leached with 20% HCl to form $AlCl_3$. The iron present also dissolves under the reaction conditions (95°C, 1 atm). The filtrate is concentrated to a 30% solids (by weight) slurry. The hydrated aluminum and iron chlorides are then removed by vacuum filtration. The aluminum chloride is decomposed at 540°C to give crude alumina. The crude alumina is then digested with NaOH at 120°C resulting in nearly complete dissolution of the alumina and leaving the iron as solids.

Pearson[6] has formulated the aluminate ion to consist of a central ion surrounded by four hydroxyl ions and two water molecules in octahedral coordination with a simple negative charge.

Here, the two water molecules may readily be replaced by two OH^- ions to form a triply negative aluminate ion $Al(OH)_6^{-3}$ which would be consistent with the precipitation of $Ca_3[Al(OH)_6]_2$.

However, Roman studies of sodium aluminate solutions[5] and studies of density-volume changes during the formation of sodium aluminate[7] support a tetrahedral coordination with a single negative charge.

This $Al(OH)_4^-$ species exists in low to moderate concentrations only. At concentrations of 15% Na_2O or more, the tetrahydroxyaluminate ion may undergo dehydration to the meta-aluminate ion, AlO_2^-.[5]

$$Al(OH)_4^- \quad AlO(OH)_2^- + H_2O \quad AlO_2^- + 2H_2O \qquad (16)$$

Between 25°C and 350°C, an equilibrium exists between the univalent ions of different degrees of hydration shown in equation (10).

The solids are removed by filtration and the filtrate is cooled and seeded with $AlCl_3 \cdot 3H_2O$ crystals. Alumina trihydrate is then formed according to:

$$2NaAlO_2 + 4H_2O \rightleftharpoons Al_2O_3 \cdot 3H_2O + 2NaOH. \quad (17)$$

The hydrate is then decomposed at 1100°C,

$$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 + 3H_2O. \quad (18)$$

5. Sinter Purification Process

Calcined clay is leached with 20% HCl at 95°C producing crude $AlCl_3$ and $FeCl_3$. The solids are removed by vacuum filtration and the filtrate is concentrated to a 30% slurry of aluminum and iron chlorides ($AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$). The crystals are then calcined at 540°C to yield crude alumina.

The crude alumina is then sintered with soda ash and limestone at 1040°C. The alumina is converted to sodium aluminate while the iron remains as solid iron oxide (Fe_2O_3).

$$Al_2O_3 + Na_2CO_3 \rightleftharpoons 2NaAlO_2 + CO_2. \quad (19)$$

The aluminate is then leached from the sinter and alumina is precipitated from the filtrate with carbon dioxide,

$$2NaAlO_2 + CO_2 + 3H_2O \rightleftharpoons Al_2O_3 \cdot 3H_2O + Na_2CO_3. \quad (20)$$

The hydrated alumina is then calcined to produce alumina.

There are several advantages and disadvantages to the hydrochloric acid processes. Among the advantages are rapid filtering rates, removal of iron, and recovery of acid.

The disadvantages include need for hydrochloric acid proof equipment, large amounts of water required, and large material requirements.

Sulfuric Acid Processes:[12]

In these processes, the silica in the raw material is not dissolved and no insoluble compounds containing silica and alumina as sulfates are formed which might cause alumina loss. However, the presence of iron will cause problems and it must be removed.

a. Electrolytic Iron-Removal Process

The starting material is calcined at 700°C to dehydrate the aluminum silicates,

$$(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) \rightleftharpoons (Al_2O_3 + 2SiO_2) + 2H_2O. \quad (21)$$

The dehydrated material is leached with a 40% solution of sulfuric acid,

$$(Al_2O_3 + 2SiO_2) + 3H_2SO_4 \quad Al_2(SO_4)_3 + 2SiO_2 + 3H_2O \qquad (22)$$

The iron present in the filtrate is removed in mercury cathode cells as metallic iron. The silica is removed from the $Al_2(SO_4)_3$ solution by heating it to 85°C and mixing with a clay residue. The solution is then concentrated by evaporation to a concentration of 40% $Al_2(SO_4)_3$. The solution is then filtered and the filtrate concentrated by evaporation to form a hydrated aluminum sulfate containing 18 moles H_2O per mole $Al_2(SO_4)_3$.

This hydrated material is dehydrated at 500°C and decomposed at 1290°C where 99.5% of the sulfur is removed,

$$Al_2(SO_4)_3 \quad Al_2O_3 + 2SO_2 + SO_3 + O_2. \qquad (23)$$

b. Chemical Iron-Removal Process

Calcined clay is leached with 40% H_2SO_4 and the pregnant liquor separated from silica residue. The iron in solution is precipitated as an iron-manganese complex by the addition of $MnSO_4$ and O_3 to the solution. The iron precipitation depends upon either the presence of free acid or excess alumina in solution. 4% excess alumina gives good iron removal.

$$Fe2(SO_4)_3 + 6MnSO_4 + 6O_3 + 12H_2O \quad 2Fe(MnO_3)_3 + 6O_2 + 9H_2SO_4 \qquad (24)$$

The iron-free solution is concentrated and filtered to remove any remaining silica. The alumina then recovered as in the electrolytic process.

c. Ethanol Purification Process:

In this process, calcined clay is leached with 40% H_2SO_4 and the leach liquor separated from a silica residue. The leach liquor concentration is adjusted to a specific gravity between 1.20 and 1.44 by evaporation of water. The aluminum sulfate solution of 88°C is then mixed with 68% ethanol at room temperature to give a two-phase system consisting of aluminum sulfate crystals in E and OH^- H_2O solution at 49°C.

The slurry temperature is raised to 68°C where subsequent cooling results in the crystallization of [$Al_2(SO_4)_3$. $16H_2O$], leaving ferric sulfate in solution. The aluminum sulfate crystals are then removed by vacuum filtration and finally decomposed to yield alumina.

The advantages of the sulfuric acid processes include:

a) nearly complete iron removal

b) the availability of well known acid proof construction materials

Disadvantages:

1. Electrolytic Process:

   a) large amount of Hg required

   b) high cost of Hg

   c) toxicity of Hg

   d) large electricity requirement

2) Chemical Iron Removal:

a) large amounts of ozone required

b) cost of ozone

c) large utility requirements

3) Ethanol Purification:

a) large amounts of make-up ethanol

b) utility requirements

c) cost of ethanol

Sulfurous Acid-Caustic Process:

A sulfurous acid-caustic process for recovering alumina has been reported by Peters and coworkers.(13)

Raw clay is calcined at approximately 700°C. It is then leached with sulfurous acid to dissolve alumina as a sulfite,

$$3H_2SO_3 + (Al_2O_3 + 2SiO_2) \rightarrow Al_2(SO_3)_3 + 3H_2O + 2SiO_2. \quad (25)$$

Iron is also converted to sulfite whereas the silica remains insoluble and is discarded.

The solution is then autoclaved at atmospheric pressure and 100°C. SO_2 is given off and a basic aluminum sulfite precipitates. The iron and other impurities may be kept in solution by having 2 moles of free SO_2 per mole of alumina.

The precipitate will be a well defined compound with the general formula:

$$Al_2O_3 \cdot 2SO_2 \cdot 5H_2O. \quad (26)$$

The monobasic sulfite may be decomposed by either calcination at 485-595°C or by a hydrothermal method.

The hydrothermal method consists of removing SO_2 by heating the slurry to between 110-160°C under 4-6 atm.

The precipitate formed is dissolved in sodium hydroxide.

$$2NaOH + Al_2O_3 \cdot (x)H_2O \rightarrow 2NaAlO_2 + (1+x)H_2O. \quad (27)$$

From this step, the trihydrate is formed then to give alumina,

$$2NaAlO_2 + 4H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 2NaOH, \quad (28)$$

$$Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 + 3H_2O. \quad (29)$$

The advantages of the sulfurous-caustic process are:

a. acid recovery

b. the $Al_2(SO_3)_3$ may be decomposed hydrothermally at 160°C

c. sulfurous acid is relatively inexpensive

Disadvantages:

a. requires pressure, digestion and decomposition

b. long reaction time for reasonable yield

c. requires closed equipment

d. acid proof equipment required

Ammonium Alum Process:

Peters and coworkers[14] have reported the evaluation of ammonium alum processes for the extraction of alumina.

The raw material is calcined at 700°C. The dehydrated clay is treated with an 85% solution of NH_4HSO_3 and 15% $(NH)_4SO_4$ at 93°C and 1 atm.

The aluminum and iron dissolve according to:

$$Al_2O_3 + 6NH_4HSO_4 \qquad Al_2(SO_4)_3 + 3(NH_4)_2SO_4 + 3H_2O. \qquad (30)$$

$$Fe_2O_3 + 6HN_4HSO_4 \qquad Fe_2(SO_4)_3 + 3(NH_4)_2SO_4 + 3H_2O. \qquad (31)$$

The iron is removed by reduction in a 50% mole solution of NH_4HSO_3 and 50% NH_4SO_3.

$$SO_2 + NH_4OH \qquad NH_4HSO_3. \qquad (32)$$

$$SO_2 + 2NH_4OH \qquad (NH_4)_2SO_3 + H_2O. \qquad (33)$$

The iron reduction may be represented by the following:

$$Fe_2(SO_4)_3 + NH_4HSO_3 + H_2O \qquad 2FeSO_4 + NH_4HSO_4 + H_2SO_4, \qquad (34)$$

$$Fe_2(SO_4)_3 + (NH_4)_2SO_3 + H_2O \qquad 2FeSO_4 + 2NH_4HSO_4. \qquad (35)$$

The reduced iron remains in solution allowing the impure alum to crystallize out of solution. Ammonium alum is purified and dissolved in 40% NH_4SO_4 solution. It is treated with 20% NH_4OH in an autoclave at 100°C to precipitate the trihydrate which then is filtered, dehydrated and decomposed.

$$(Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O) + 6NH_4OH \qquad (Al_2O_3 \cdot 3H_2O) + 4(NH_4)_2SO_4 + 24H_2O. \qquad (36)$$

Potassium Alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$] Process:

A potassium alum process for aluminum extraction has been evaluated by Peters and coworkers.[15]

Raw clay is dehydrated and leached with a sulfuric acid-potassium sulfate solution countercurrently at approximately 90°C.

$$(Al_2O_3 + 2SiO_2) + 3H_2SO_4 + K_2SO_4 + 21H_2O \quad K_2SO_4 \cdot Al_2O_3 \cdot 3SO_3 \cdot 24H_2O + 2SiO_2. \qquad (37)$$

The solution is then filtered to remove the silica residues. Iron removal is affected by reduction of the iron with sulfur dioxide. The ferrous iron formed then remains in solution during alum crystallization. Iron present in the recycle solution is oxidized and precipitates during leaching when excess clay is added to the leach system.

The potassium alum is crystallized in vacuum crystallizers at 20°C, leaving impurities such as Ti, Ca, P, Ca, Fe, Na and Mg in solution. The alum crystals are then separated from the mother liquor in centrifugal filters and washed.

The alum is decomposed in autoclaves at 200°C for 30 minutes with 4 1/2 pounds of 250 psig steam for each pound of alum present,

$$3(K_2SO_4 \cdot Al_2O_3 \cdot 3SO_3 \cdot 24H_2O) \quad K_2SO_4 \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O + 5H_2SO_4 + 2K_2SO_4 + 58H_2O. \qquad (38)$$

The basic potassium alum is fed to furnaces where the cyrstals are first dehydrated at temperatures less than 600°C,

$$(K_2SO_4 \cdot 3Al_2)_3 \cdot 4SO_3 \cdot 9H_2O) \quad K_2SO_4 \cdot 3Al_2O_3 \cdot 4SO_3 + 9H_2O. \qquad (39)$$

The decomposition is continued at temperatures between 600°C-800°C,

$$(K_2SO_4 \cdot 3Al_2O_3 \cdot 4SO_3) \quad 3Al_2O_3 + K_2SO_4 + 4SO_3. \qquad (40)$$

The remaining iron is removed by reduction with SO_2. The ferrous ion remains in solution during alum crystallization.

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